# Comparison of Spectrolyser Device Measurements with Standard Analysis of Wastewater Samples in Novi Sad, Serbia

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# Assessment of the point source impact pollution from the wastewater discharge into the Danube River in the city of Novi Sad, Serbia

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## Abstract

On-line monitoring was performed using spectrolyser equipment, coupled with laboratory analysis for samples collected from wastewater discharge in the city of Novi Sad, Serbia, during first 24h of three and 48h of six monitoring campaigns from December of 2012 to April of 2013. Significant correlation with $R^2 > 0.9$ was observed between laboratory analysis and spectrolyser measurements. COD/$BOD_5$ ratio in combined industrial and municipal wastewater ranged from 1.2 to 2.0 indicating the presence of biodegradable organic matter which could be easily removed using aeration treatment process. Micro/trace element and/or heavy metals in wastewater samples were within the limits as per the standard prescribed for wastewater, and should not pose any serious hazard risk. However BOD, COD, ammonia and total phosphorus concentrations were measured above the limit value according to Serbian and EU legislation and should be reduced before discharging wastewater directly into the Danube River.

**Keywords:** spectrolyser, chemical and biological oxygen demand, wastewater

## 1. Introduction

The quality of the surface water is a significant problem in many regions of the world. It can frequently limit the use of this essential resource and, in more extreme circumstances, harm human health, biota and environment. Some studies of water quality in various effluents (Meybeck 2002; Hanrahan et al. 2003; Astel et al. 2007; Simeonov et al. 2003; Dawe 2006) revealed that anthropogenic activities have an important negative environmental impact on water quality in the downstream sections of the major rivers. This is a result of cumulative effects from upstream development but also from inadequate wastewater treatment (Popa et al. 2012). Water quality decay, characterized by important modifications of chemical oxygen demand (COD), total suspended solids (TSS), total nitrogen (TN), total phosphorous (TP), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), and so forth are the result of wastewater discharge into the rivers (Popa et al. 2012). Wastewater discharges from sewage and industries are major components of water pollution, contributing to oxygen demand and nutrient loading of the water bodies, leading to a destabilized aquatic ecosystem (Morrison et al. 2001).

Recent environmental legislation implies the need for optimization of wastewater treatment and, therefore, a need for tools which provide quantitative and qualitative information on municipal wastewater characterization and evolution (Vaillant 2002). One of main tasks conducted by European Water Framework Directive (WFD) (Petrescu et al. 2012) is continuous monitoring of the water regime, together with the determination of the water quantity and quality, which provides a relevant source of information in presenting the state of

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water resources in real time. Also, the analysis of the surface water quality is fundamental for a sustainable management of water resources. Even though, the directive does not introduce innovative devices for quality control as well as on-line measurements, automated technologies contribute to improve monitoring of water in terms of a new approach to water monitoring. Moreover, on-line monitoring allows the implementation of policies intended to reduce pollution load, improve controls on industrial discharges into the network (Thomas and Pouet 2006) and, as a result of reducing the overall pollution burden, protecting the WWTP and network equipment. Accidental discharges can have a damaging effect on the biological processes involved in wastewater treatment and if not adequately treated, can pass through the treatment system and into the receiving waters where it can have a harmful effect on the environment and eventually reach the sources of potable water supplies causing taste and odor problems in the supply of drinking water (Bourgeois et al. 2003).
Within the framework of research, for the first time in the city of Novi Sad, continuous optical on-line monitoring system was introduced using Spectrolyser device (S::CAN, Austria, Vienna) for *in situ* measurements, which allows continuous measurement of basic physicochemical characteristics of wastewater ($BOD_5$, COD, $NO_3$-N, TSS, SAC254 and SAC436) at each measuring point. Data obtained by these measurements were complemented with an accredited laboratory analysis, in order to complete observation of the Danube raw water real status on the selected site. During the measurement campaign on-line sampling in winter 2012/13 and spring 2013 (December - April) samples were collected three times a day, for a period of 24h of three and 48h of six monitoring campaigns. Analysis of the basic physico - chemical parameters and the concentrations of metals was performed in accredited Laboratory for monitoring of landfills, waste water and air.

## 2. Material and methods

On-site monitoring was performed using s::can spectro::lyser (S::can Messtechnik, Vienna, Austria) on sampling site GC 2 (19° 51' 25,139" E, 45° 15' 44,581" N), which is one of four sewage discharges in Novi Sad where the greatest amount of industrial wastewater is discharged directly into Danube river, indicating the greatest impact on the variation of the Danube river pollution. Basin pump station GC2 covers the northern half of the city (size about 900 ha). In this area there are about 100,000 inhabitants.
Continuous measurement of basic physicochemical characteristics of wastewater ($BOD_5$, COD, $NO_3$-N, TSS, SAC254 and SAC436) was performed every 15 min. Nine sampling campaigns were conducted during five months in winter 2012/13 and spring 2013. During first 24h and 48h of continuous monitoring samples for laboratory analysis were collected three times per day at 6:00h, 14:00h and 22:00h. Data for average daily temperature, humidity and precipitation during nine sampling campaigns in 2012/13 were obtained from Republic Hydrometeorological Service of Serbia.
Wastewater samples for laboratory analysis were collected from GC 2 sampling site in the city of Novi Sad in sealed 1L glass bottles, stored in hand refrigerator at 4 $^{o}$C, and transported to the laboratory. Samples were analyzed for oxygen ($BOD_5$, COD, dissolved oxygen, permanganate index), nutrients (ammonium, nitrite, nitrate, total phosphorus), conductivity, sulfate concentrations and the concentrations of metals: Pb, Fe, Cd, Cr, Ni, Zn, according to the Standard Methods for the Examination of Water and Wastewater (Eaton and Clesceri 2005). Conductivity and dissolved oxygen were determined *in situ* using portable Multi 340i WISSENSCHAFTLICH – TECHNISCHE WERKSTATTEN GMBH device. Biological oxygen demand ($BOD_5$) was determined using the BODTrak™ method. The HachBODTrak apparatus is based on the manometric principle of operation. The chemical oxygen demand, ammonium, nitrite, nitrate, total phosphorus and sulfate concentrations were measured with

UVVIS spectrophotometer (DR 5000, HACH, Germany). In order to verify the precision and accuracy of the methods, the certified reference materials Demand WP, Simple nutrients WP, Complex nutrients WP (RTC, UK) have been used.

For the determination of metals, wastewater samples were subjected to digestion, spiked with 5ml of $HNO_3$ using the microwave assisted digestion system MWS-3+ (Berghof, Germany) and analyzed using Thermo atomic absorption spectrometer with hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air-acetylene flame with addition of nitrogen suboxide flame for Cr. The recoveries were carried out by the addition of the standards of each element at different levels. Blanks were included in each batch of analysis. Accuracy was evaluated with the certified reference materials LGC6175 (LGC, UK) and SPS-WW2 Batch 110 (SPS, Norway). Recoveries ranged from 89 % to 97 %. Calibration curves for the determination of metals were processed with different dilutions of the standard stock solutions conc. 1000 mg/l (J.T: Baker, The Netherlands); the linear regression lines were obtained with $R \geq 0.95$.

The Data were processed using software ana::pro for s::can spectro::lyser. Correlations between the data obtained in on-line monitoring and laboratory analysis for $BOD_5$ and COD concentrations were analyzed using Pearson's correlation coefficients by IBM SPSS software (a significance threshold of $p=0.01$ was retained).The influence of meteorological data on pollutant concentrations in wastewater was also evaluated using IBM SPSS software.

## 3. Results and discussion

### *3.1. Laboratory results*

The concentration ranges of basic physicochemical parameters and metals were presented in table 1. The highest concentrations were obtained for ammonia, biological and chemical oxygen demand. Electrical conductivity ranged from 568 to 4450 mg/l, indicating the high salinity of wastewater. The limit value for total phosphorus (2 mg/l) and total nitrogen (15 mg/l) according Serbian and EU legislation has been exceeded in the most of analyzed samples since ammonia concentrations were in range 13.7 – 60.4 mg/l.

Table 1.Concentration ranges of metals and basic physicochemical parameters in wastewater samples (n=43)

| **Parameter** | **Min-Max** | **Mean±SD** |
|---|---|---|
| **Conductivity (μS/cm)** | 568-4450 | 1362±746 |
| **D.O. (mg/l)** | 0.07-3.57 | 0.90±0.72 |
| **$BOD_5$(mg/l)** | 100-614 | 369±134 |
| **COD(mg/l)** | 196-839 | 556±192 |
| **$NO_3^-$ (mg/l)** | 0.1-0.5 | 0.3±0.1 |
| **$NO_2^-$ (mg/l)** | 0.01-0.17 | 0.05±0.04 |
| **$NH_3$ (mg/l)** | 13.7-60.4 | 37.8±11.1 |
| **Total P (mg/l)** | 1.6-8.7 | 4.6±1.2 |
| **$SO_2^{-4}$ (mg/l)** | 35-128 | 63±22 |
| **Permanganate index (mg/l)** | 10.1-81.1 | 48.1±16.8 |
| **Cr (mg/l)** | <0.1 | |
| **Pb (mg/l)** | 0.01-0.15 | 0.06±0.03 |
| **Fe (mg/l)** | 0.3-9.9 | 1.5±1.7 |
| **Cd** | <0.005 | |
| **Ni** | 0.04-0.12 | 0.09±0.02 |
| **Zn** | 0.03-0.51 | 0.17±0.11 |

The analytical measurement data for Cr and Cd were under limits of detection (LOD) in all mixed wastewater samples. The analysis for micro/trace element and/or heavy metals in mixed wastewater samples shows that Zn, Fe, Pb, Cd, Cr and Ni are well within the limits as per the standard prescribed for communal wastewater and should not pose any serious hazard risk.

Average daily values of COD and $BOD_5$ were 556±192 and 369±134 mg/l, respectively. Directive Councile Directive (91/271/EEC) and the Regulation on limit values of pollutants in water and deadlines for their achievement (Official Gazette of the Republic of Serbia, No. 67/2011 and 48/2012) prescribes threshold limit values for the parameters COD and $BOD_5$ in the wastewater discharged into the surface waters as125 and 25 mg/l, respectively. COD and $BOD_5$ were measured in all mixed wastewater samples above the prescribed limits.

The reduction of $BOD_5$ and COD in the separate treatment units of a plant can be used to measure the efficiency of each unit in the wastewater treatment process. It is very important to calculate the ratio of COD/BOD5 because it indicates the biodegradability of wastewater. The higher the ratio is the less the biodegradability of the wastewater. Ratio values depend on the nature of the wastewater and the COD/$BOD_5$ ratio value for municipal raw wastewater is in the range from 1.25 to 2.5, whereas for industrial wastewater the ratio goes up to 10 or more. COD/$BOD_5$ ratio in combined industrial and municipal wastewater samples analyzed in this study ranged from 1.2 to 2.0 indicating the higher quantity of municipal wastewater compared to industrial wastewater and therefore high ability of wastewater to biologically degrade.

Total organic load of the wastewater at discharge GC 2 in kg COD/day and kg BOD/day was calculated on the basis of the average daily flows data (540 – 800 l/s) and results were shown in figure 1. COD loads ranged from 2073 l to 37809 kg/day, while BOD loads of wastewater were in range 13033 – 24791 kg/day.

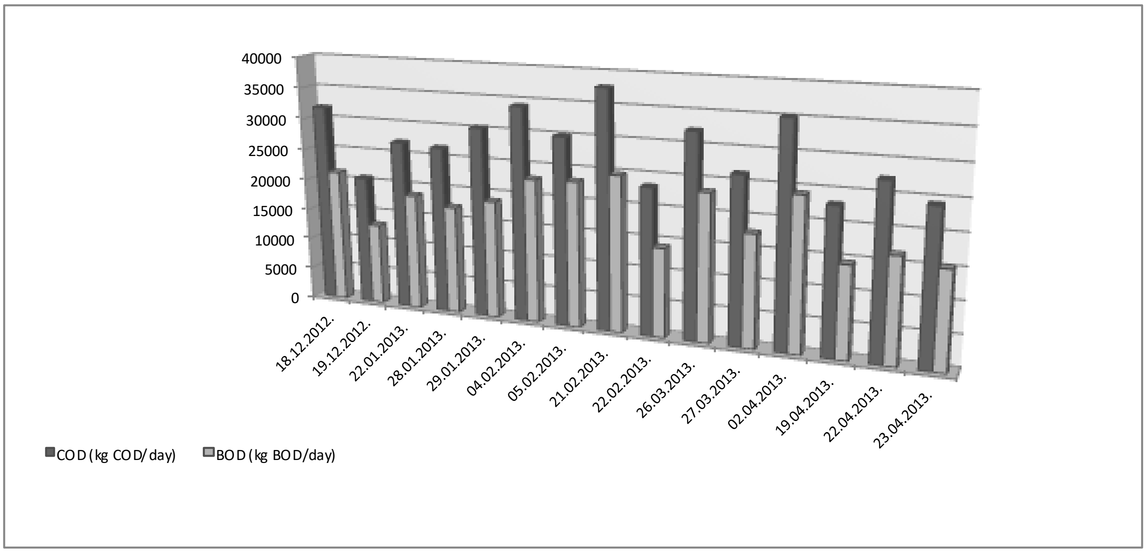


Figure 1.Total daily organic load of the wastewater at discharge GC 2

*3.2 Continuous monitoring results*

Data were obtained for COD, BOD, SAC254 and SAC436 every 15 minutes in all sampling campaigns. Studies have shown that during stable temperature and precipitation conditions SAC parameters are compatible with COD and BOD parameters. It can be concluded that COD and SAC254, and BOD and SAC 436 are compatible with the same trendline and fluctuations, respectively. For the period from January 28$^{th}$ until February 2$^{nd}$ 2013, according to data obtained from Republic Hydrometeorological Service of Serbia, temperature and precipitation were higher than normal for that part of the year, which can be noticed by diverging of trendlines of parameters for mentioned sampling period. High temperature (extreme) and normal precipitation levels for sampling campaign in April have shown an interesting and unexpected behavior of measured parameters. During unstable weather conditions values of parameters COD/BOD/SAC were drastically varying. Online monitoring curves for $BOD_5$ and COD showed periodic trends with peak minimum between 4:00 h and 7:00 h and two peaks maximum between 13:00 h and 17:00 h as well as 20:00 h and 00:00 h. $NO_3^-$ concentrations were under limit of detection (LOD) in all sampling campaigns.

For overall data from 5 months period of monitoring it can be noticed that trendlines ($R^2$) and shape of the parameters curve for COD/BOD and SAC correspond. Two correlations can be noticed CODeq/SAC436 and BODeq/SAC254. SAC parameters represent communal organic load of water, while CODeq and BODeq detect industrial and agricultural organic load in the effluent, respectively. As the sewerage system of Novi Sad is mixed sewerage system collecting communal, industrial and small amount of agricultural wastewater; the main conclusion from data evaluation that can be derived for monitoring period is that SAC parameters show ‘clean’ flow of communal wastewater organic load, while CODeq and BODeq have periodical picks (extremes) that can be only explained as human behavior routines, as well as high load of industrial and agricultural effluents to sewerage system, respectively.

*3.3 Correlation between online monitoring and laboratory analysis*

Statistical analysis of obtained results indicated good correlation between on-line continuous measurements and laboratory analysis. Within nine sampling campaigns during winter period 2012/13 and spring 2013, linear curves were obtained for COD and $BOD_5$ with $R^2$ of 0.931 and 0.903, respectively. Pearson correlation coefficients (r) showed positive correlations with values 0.910 (p=0.01) and 0.657 (p=0.01) for COD and $BOD_5$, respectively. Better correlation was obtained for COD, because of difference in measuring BOD. Using on line measuring equipment obtained values for BOD are for every moment of time and in laboratory conditions the $BOD_5$ levels were determined. The total suspended solids (TSS) concentrations were not measured in laboratory conditions, so measuring data are obtained using S::can UV probe. These results were not included into the evaluation process, during this particular study.

*3.4. The impact of seasonal condition variations and meteorological parameters on the quality of wastewater*

The analysis of the seasonal variations and the meteorological parameters influence on the quality of the wastewater showed a significant effect of humidity on the dissolved oxygen concentrations (Table 2). The results obtained for dissolved oxygen showed daily variations that may result from activities of aquatic organisms; the minimum is registered in the early morning hours and maximum in the early afternoon when the water temperature is the highest. The concentration levels of sulfate showed the dependence of the air and water temperature while a concentration of iron depends just on the levels of a water temperature.

Precipitation has a significant effect on the majority of measured values of electrical conductivity, dissolved oxygen, ammonium, COD and total phosphorus. It could be concluded that seasonal variations such as changes in precipitation and changes in air and water temperatures have a significant impact on the quality of wastewater. Correlation matrix with the values of the Pearson coefficients with highlighting the significant correlations with the probability of 95% and 99% are shown in Table 2.

Table 2. Correlation matrix of the influence of meteorological parameters on the quality of wastewater

| | **Conduct.** | **D.O.** | **$NH_3$** | **Total P** | **Perm. index** | **COD** | **$BOD_5$** | **Sulfate** | **Fe** |
|---|---|---|---|---|---|---|---|---|---|
| **Air temp.** | -0.252 | -0.262 | 0.019 | -0.035 | 0.397 | -0.143 | -0.254 | **0.761(**)** | -0.434 |
| **Humidity** | 0.424 | **0.555(*)** | -0.460 | -0.372 | -0.005 | -0.147 | -0.133 | -0.392 | 0.396 |
| **Precipitation** | **0.779(**)** | **0.718(**)** | **-0.614(*)** | **-0.549(*)** | -0.217 | **-0.554(*)** | -0.452 | -0.287 | 0.439 |
| **Water temp.** | -0.453 | -0.460 | 0.376 | 0.244 | 0.204 | 0.087 | -0.035 | **0.648(**)** | **-0.611(*)** |

**(**) Correlationissignificantat the level p = 0.01**
**(*)Correlationissignificantat the levelp = 0.05**

Average monthly concentrations of selected parameters in the effluent during the sampling period from December of 2012 until April of 2013 were calculated and the next conclusions were derived. In the campaign conducted in February, lower concentrations values of various parameters were observed in comparison with previous campaigns in December and January as a result of dilution effect due to melting of snow. In March, during the period of highest rainfall and high humidity, conductivity reached a maximum value of two times greater than in other months of the campaign, while the minimum value was measured for phosphorus content. In April of 2013, during the dry period of the year with the lowest humidity and highest temperatures in comparison with the previous series of measurements, the concentration of sulfate reached a maximum value.

## 4. Conclusions

Data obtained within the monitoring program provide insight into detailed influence of mixed urban (industrial and communal) and agricultural wastewater discharges onto the Danube River surface water quality, which contributes to better identification of the pollutant loads, creating the basis for risk assessment and ultimately establishing standards of chemical quality, as well as a good basis for future wastewater treatment plant design and improvement. The great importance of this study is reflected in the fact that continuous on-line monitoring of wastewater using an optical system, Spectrolyser device is introduced for the first time in the city of Novi Sad, providing continuous measurements of basic physical and chemical characteristics of wastewater ($BOD_5$, COD, TSS, SAC254, SAC436) at each time point. The data obtained in this way are supplemented by laboratory analysis using standard testing methods in order to get more comprehensive review of the real status of wastewater discharged directly into Danube River on the selected site. Results of laboratory analysis parameters of biological and chemical oxygen demand indicated good correlations with the results obtained with on-line measurement, with $R^2 > 0.9$, thus confirming the efficiency of continuous measurement with spectrolyser equipment. It could be concluded that this equipment as time and cost effective tool can be used for continuous on-line monitoring of communal wastewater.

The study clearly indicates that some of the physicochemical and heavy metal parameters undertaken to assess the water quality of wastewater discharge were found below the prescribed limit (Zn, Cd, Cr and Ni), which indicates a low risk level for negative environmental effects induced from occurrence of toxic metals, while some parameters were measured above the appointed regulation limits ($BOD_5$, COD, ammonia, total phosphorus). $COD/BOD_5$ values indicating the presence of higher biodegradable organic matter which could be effectively removed with appropriate design of aeration treatment process. High biodegradability of wastewater according to $COD/BOD_5$ ratio improves the efficiency of subsequent biological treatment.

It is well known that wastewater is a huge problem, even in developed countries, for environmental protection from chemical and other sanitary risks to human health. That is the reason why research on wastewater quality has to be encouraged with development of on-site measurement methods. The design and implementation of future monitoring programs of wastewater in the city of Novi Sad using on-line device as early warning system, would give information that will enable timely, effective and appropriate actions to prevent further degradation of the Danube River surface water quality and possible negative effects on aquatic life. The obtained monitoring data will be used for implementation of modern approach to wastewater treatment processes and plant design as a principle of good practice and to propose the most appropriate method for collection, transport, treatment and discharging of effluent into the recipient, the Danube River.

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